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Reduction of 1-Substituted 2,4,6-Triphenylpyridinium Ions in Aprotic Media

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Some 1-substituted 2,4,6-triphenylpyridinium salts have been studied by cyclic voltammetry. The compounds exhibit two or three reduction peaks depending on the sweep rate and the rate of loss of the 1-substituent. The rate of cleavage of the one-electron reduction product (the radical) was measured by cyclic voltammetry and double potential step chronoamperometry, and the rate of cleavage of the two-electron reduction product (the anion) found by simulation of the voltammetric curves; the simulation suggested that the rate of cleavage of the radical was faster than the rate of cleavage of the anion. This unexpected finding is tentatively explained by different conformations of the phenyl groups in the 2 and 6 positions in the radical and in the anion.

Some years ago it was found that the reaction between 1-alkyl-2,4,6-triphenylpyridinium ions and nitroalkane anions resulted in *C*-alkylation of the nitronate,[1,2] and this finding was followed by a series of investigations of substitution reactions having 2,4,6-triarylpyridine as the leaving group.[3]

The mechanism of the *C*-alkylation of the nitroalkane anion in the substitution reaction with 2,4,6-triphenylpyridine (TP) as the leaving group was suggested to involve a non-chain radical reaction with a radical pair or a charge-transfer complex on the reaction path;[4] one reason for assuming a radical reaction was that, in the $S_{RN}1$/S_N2 competition in the reaction of nitronate ions with benzyl halides, *C*-alkylation was found when radicals were involved, whereas the S_N2 reaction resulted in an *O*-alkylation.[5]

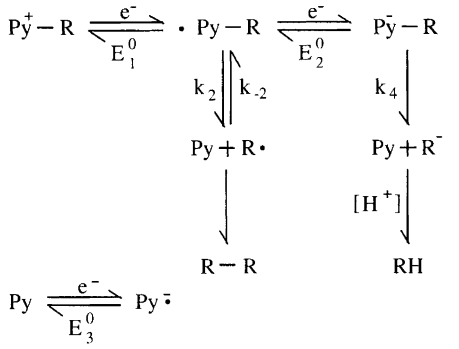
The electrochemistry of some *N*-benzyl- and *N*-allylpyridinium salts substituted in the 2-, 4- and 6-positions was investigated by Grimshaw *et al.*[6] It was found that the reduction potentials of the pyridinium salts were significantly more negative than the oxidation potential of the nitronate ion, so an outer-sphere electron transfer from the anion to the pyridinium compound was endergonic. It was also found that the rate of cleavage of 1-benzyl-2,4,6-triphenylpyridinium radical was 240 ± 50 s^{-1} and the cleavage of the other radicals measured was slower. A fast cleavage reaction which might have made the electron transfer plus cleavage exergonic was thus not found. Eberson estimated[7] a rate constant for an outer-sphere electron transfer from 2-nitropropane anion to 1-benzyl-2,4,6-triphenylpyridinium ion in DMSO to be 10^{-13} M^{-1} s^{-1} using the Marcus equation.

Our interest in the reduction of substituted pyridinium compounds is connected with the use of anions as electron donors. 1-Methyl-2,4,6-triphenylpyridinium salts are reduced during cyclic voltammetry (CV) in two reversible one-electron reductions to the anion of 1,4-dihydro-1-methyl-2,4,6-triphenylpyridine which is not cleaved in the timescale of CV; on reaction of this anion with *tert*-butyl bromide, *tert*-butylation took place in the 4-position and the reaction of the anion with benzyl bromide likewise gave benzylation in the 4-position.[8] A preliminary investigation of 1-benzyl-2,4,6-triphenylpyridinium (BTP^+) perchlorate suggested that the two-electron reduction product, the anion, cleaved more slowly than the radical. This was contrary to our expectation, as a two-electron reduction product, at least in the case of dianions, cleaves faster than a one-electron product, and a more thorough investigation of BTP^+ and other 1-substituted 2,4,6-triphenylpyridinium salts was made.

Results and discussion

The following 1-R-2,4,6-triphenylpyridinium salts were investigated: R = isopropyl ($iPTP^+$), benzyl (BTP^+), 4-methylbenzyl ($MBTP^+$), 4-chlorobenzyl ($ClBTP^+$), 4-methoxybenzyl ($MOBTP^+$), allyl (ATP^+) and phenyl (PTP^+).

Cyclic voltammetry (CV) was carried out in DMF–0.2 M $TBABF_4$. The rather high concentration of supporting electrolyte was chosen to diminish the ohmic resistance. The iR-compensation was adjusted at each sweep rate so the reversible redox system ferrocene showed a peak separation of 59 mV at 25°C.



Scheme 1.

All the compounds investigated, except PTP^+, showed three redox reactions with peak heights depending on experimental conditions. The first peak corresponded to the reduction of the pyridinium compound to the radical, the second peak to the reduction of this species to the anion, and the third redox reaction was that of 2,4,6-triphenylpyridine formed by cleavage of the radical or the anion (Scheme 1; in the scheme Py stands for 2,4,6-triphenylpyridine).

In Fig. 1 the CV of BTP^+ is shown for different scan rates v and different switching potentials. At $v = 10$ V s^{-1} the first peak is irreversible and only a small second peak is visible, whereas the third peak is large and reversible. Under these conditions the cleavage of the radical is nearly complete when the potential reaches the value of the second reduction. At $v = 100$ V s^{-1} and switching potential between the first and the second reduction the first reduction is close to reversibility; changing the switching potential to a value between the second and third peak shows the second reduction also to have some chemical reversibility, but the peak separation suggests a quasi-reversible reaction. Under these conditions the third peak is slightly smaller than the second peak.

Fig. 2 shows in a similar way CV of $iPTB^+$. At slow sweep rate (0.1 V s^{-1}) the first redox reaction is irreversible, the second one looks a little more reversible and the third one is reversible. At 5 V s^{-1} both the first and the second reductions are reversible and the third one is almost not observed, as the cleavage of both the anion and the radical is too slow to give an appreciable concentration of 2,4,6-triphenylpyridine (TP).

A preparative reduction of BTP^+ at the potential of the first wave gave TP and bibenzyl in a one-electron reaction as reported by Grimshaw *et al.*;[6] no toluene or tributylamine was detected, but a low yield (about 1%) of

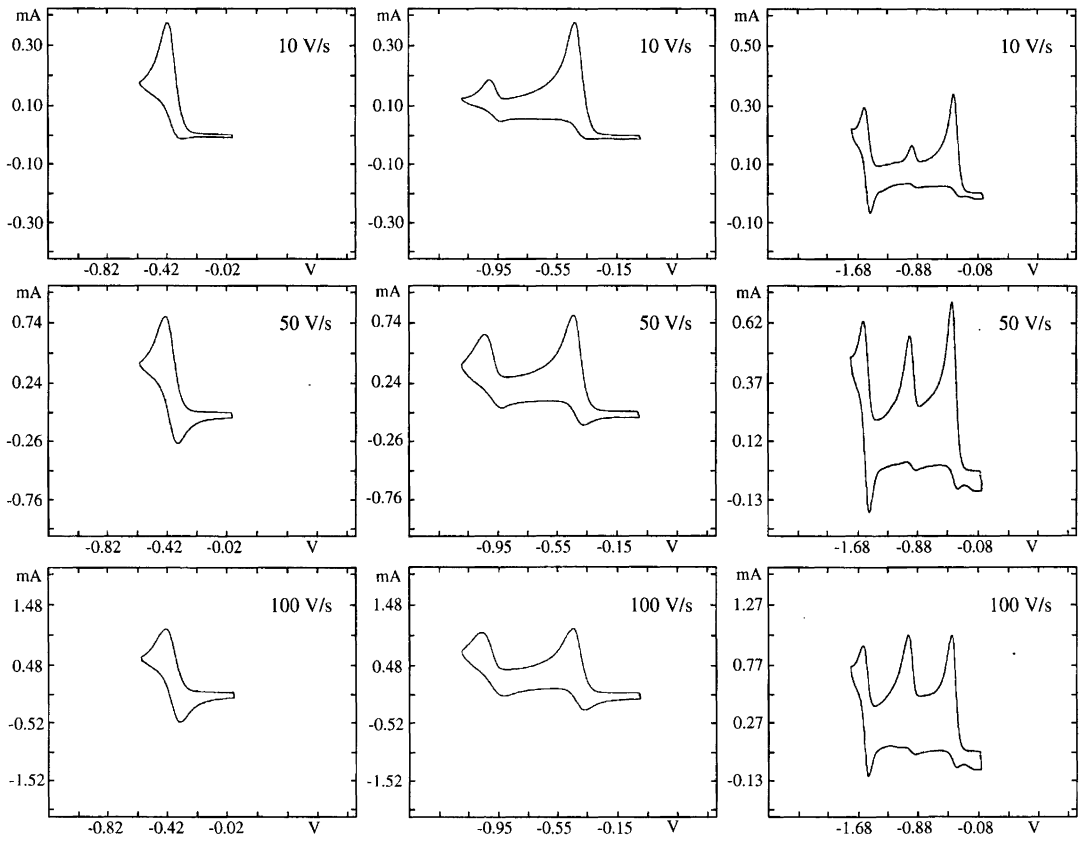


Fig. 1. Cyclic voltammograms at a 0.6 mm gold electrode of 1-benzyl-2,4,6-triphenylpyridinium perchlorate in DMF–0.2 M $TBABF_4$, reference electrode Ag/AgI, 0.2 M $TBABF_4$. Sweep rates: (a) 10 V s^{-1}; (b) 50 V s^{-1}; (c) 100 V s^{-1}. The switch potentials are: left, between 1st and 2nd reduction; middle, between 2nd and 3rd reduction; right, potential negative of the 3rd reduction.

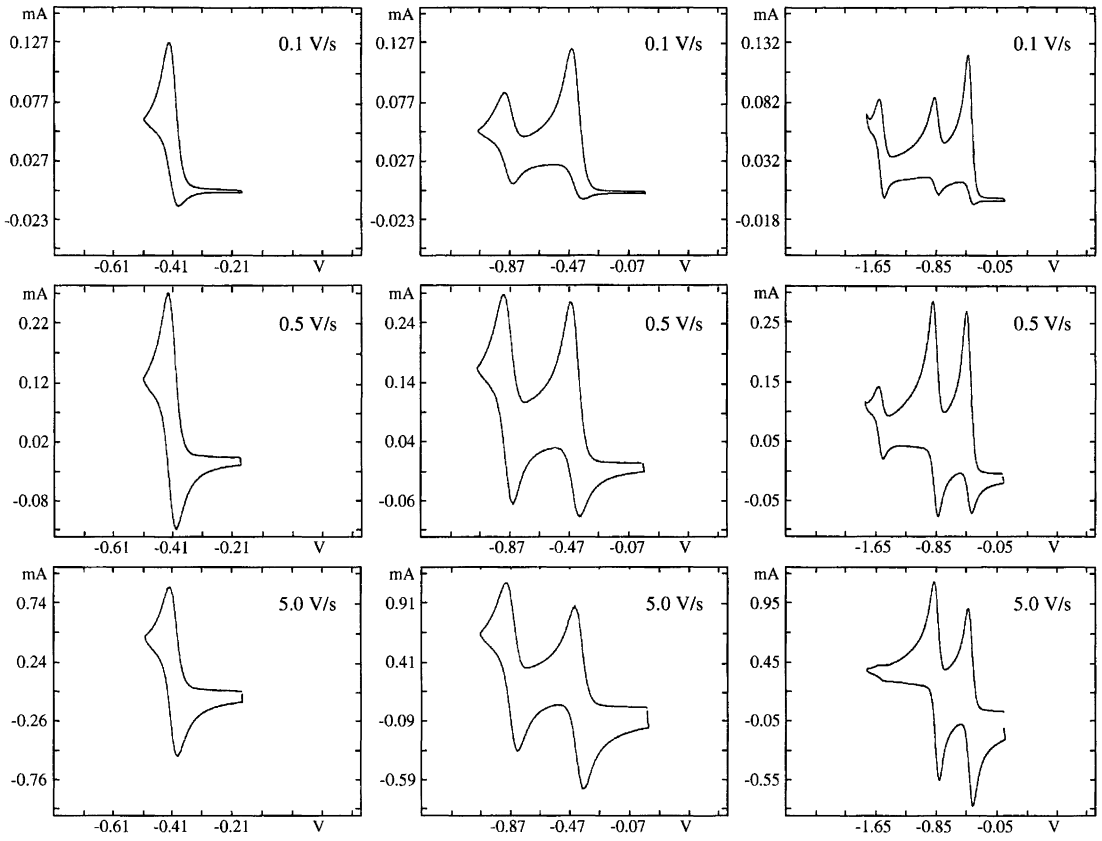


Fig. 2. Cyclic voltammograms at a 1.0 mm gold electrode of 1-isopropyl-2,4,6-triphenylpyridinium perchlorate in DMF–0.2 M $TBABF_4$; reference electrode Ag/AgI, 0.2 M $TBABF_4$. Sweep rates: (a) 100 mV s^{-1}; (b) 500 mV s^{-1}; (c) 5 V s^{-1}. Switch potential: left, between 1st and 2nd reduction; middle, between 2nd and 3rd reduction; right, potential negative of the 3rd reduction.

benzylated bibenzyls was found. A yellow colour, however, indicated the presence of a small amount of unidentified by-products.

The reaction scheme for the reduction and cleavage of a 1-substituted 2,4,6-triphenylpyridinium salt $(RTP)^+$ could, *a priori*, involve reactions (1)–(17).

$$RTP^+ + e^- \rightleftarrows RTP^\bullet \qquad E_1^\circ \qquad (1)$$

$$RTP^\bullet \overset{k_2}{\rightarrow} TP + R^\bullet \qquad (2)$$

$$RTP^\bullet + e^- \rightleftarrows RTP^- \qquad E_2^\circ \qquad (3)$$

$$RTP^- \overset{k_4}{\rightarrow} TP + R^- \qquad (4)$$

$$TP + e^- \rightleftarrows TP^{-\bullet} \qquad E_3^\circ \qquad (5)$$

$$R^\bullet + R^\bullet \overset{k_6}{\rightarrow} R\text{–}R \qquad (6)$$

$$RTP^\bullet + R^\bullet \rightarrow RTP^+ + R^- \qquad (7)$$

$$R^\bullet + e^- \rightleftharpoons R^- \qquad E_4^\circ \qquad (8)$$

$$RTP^- + R^\bullet \rightarrow RTP^\bullet + R^- \qquad (9)$$

$$R^\bullet + HS \rightarrow RH + S^\bullet \qquad (10)$$

$$R^- + H^+ \rightarrow RH \qquad (11)$$

$$R^- + Bu_4N^+ \rightarrow Bu_3N + RH + \text{butene} \qquad (12)$$

$$R^- + RTP^+ \rightarrow R\text{–}R + TP \qquad (13)$$

$$RTP^\bullet + RTP^\bullet \rightarrow (RTP)_2 \qquad (14)$$

$$RTP^\bullet + RTP^+ \rightarrow (RTP)_2{}^{+\bullet} \qquad (15)$$

$$RTP^\bullet + HS \rightarrow RTPH + S^\bullet \qquad (16)$$

$$RTP^- + H^+ \rightarrow RTPH \qquad (17)$$

A number of these reactions were found insignificant for the reasons given below and were thus not included in the simulations of the CV curves. Reaction (7) was excluded because the reduction potential (E_R°.) of the benzylic radicals[9,10] and of the alkyl radicals is 0.5 V and 1.5 V, respectively, more negative than E_1°; an electron transfer from $R^\bullet$ to $RTP^\bullet$ [the reverse of reaction (7)] is unlikely, as the oxidation potential of the benzyl radical[9] is 1 to 1.5 V more positive than the reduction potential of RTP^+; reduction of $R^\bullet$ at the electrode (8) is insignificant, as k_2 is rather low, so the cleavage takes place relatively far from the electrode and back-diffusion to the electrode is unlikely during the lifetime of the radical.

Reduction of $R^\bullet$ by RTP^- (9) is strongly endergonic for alkyl radicals, but only slightly endergonic (2–3 kcal) for benzylic radicals. Fast protonation of R^- could drive the reaction, but as this should have given rise to an increase in the peak height of the second reduction wave, which was not observed, reaction (9) was not included in the simulation. No toluene and tributylamine [reactions

(11) and (12)] were detected by GLC under preparative conditions so this reaction was also neglected.

Hydrogen abstraction by benzyl radicals is slow on the CV timescale, so reaction (10) was neglected in the simulation. If any toluene is formed in the preparative reduction of BTP^+ at the potential of the first reduction (−0.5 V vs. Ag/AgI), which is not negative enough to reduce the benzyl radical to the benzyl anion, it is probably formed by reaction (10); the timescale in a preparative reaction is sufficient to allow hydrogen abstraction even by benzyl radicals. The S_N2 reaction (13) would not occur because the homogeneous electron transfer from R^- to RTP^+ yielding $R^\bullet$ and $RTP^\bullet$ would be diffusion-controlled. Reactions (14) to (17) might be responsible for the formation of the low yield of unidentified by-products found under preparative conditions, but the yield was so low that the reactions could not influence the voltammetric curves.

A complication could arise if the cleavage of $RTP^\bullet$ (2) was reversible and k_{-2} comparable to k_2. CV was therefore carried out in the presence of (a) cumene and (b) acrylonitrile to investigate whether a removal of $R^\bullet$ would influence the CV curves. Cumene is a good hydrogen atom donor, and even benzyl radicals should be able to abstract hydrogen from cumene at a sufficiently high rate to influence the voltammetric curves; alkyl radicals react reasonably fast with acrylonitrile[11] and it was shown that reduction of anthracene in the presence of butyl chloride and acrylonitrile produced a fair yield of heptanonitrile.[12] Addition of a large excess of either cumene or acrylonitrile had no influence on the CV curves of BTP^+, so the possible reversibility of (2) is insignificant in this connection.

The voltammetric curves were simulated using the program ELEC. The program required the reversible potentials E_1°, E_2° and E_3°, which could be measured at suitable scan rates, and further the known switching potentials, the rate constants sought for the cleavage reactions, the rate constants for the heterogeneous electron transfer (k_{het}) and the corresponding α-values. Reactions (1) to (5), which were found important for the curves, were included in the simulations.

For reaction (1) $\delta E_p(\delta \log v)^{-1} = -29.9$ mV decade^{-1} which is in accordance with reactions (1) + (2) being an EC process. Benzyl radicals are formed in the cleavage as indicated by the formation of bibenzyl and benzylated bibenzyls. The peak separation for (1) indicated a large (> 1 cm s^{-1}) heterogeneous rate constant. The rate constant k_2 was then determined by fitting simulated curves with the experimental ones with a switching potential between the first and the second reduction.

When k_2 was determined k_4 could be found by simulation of eqns. (1)–(5), when the heterogeneous rate constants and α were known. k_{het} for the first and third reductions were sufficiently high not to influence the cyclic voltammetric curves at $v \leq 100$ V s^{-1}; the second reduction [eqn. (3)] became quasi-reversible at high scan rates. The apparent k_{het} was determined from the peak separation[13] at high sweep rates; the iR-compensation was adjusted from the peak separation of ferrocene at the same sweep rate.

The transfer coefficient α could influence the shape of the curves, but preliminary simulations showed that, with the sweep rates used and taking into account the uncertainty of the determination of the heterogeneous rate constants, the influence of α on the curves was smaller than that caused by the uncertainty in the determination of k_{het}, as long as $0.3 < \alpha < 0.7$. The transfer coefficient was thus assumed to be 0.5 in the simulations.

The rate of the cleavage k_2 was also determined by double potential step chronoamperometry (DPSC) using simulated working curves. The uncertainty of the method was slightly larger than for CV; similar results were obtained by both methods.

In Table 1 k_2 for (2), k_4 for (4), and the apparent heterogeneous rate constant k_{het} for (3), E_1°, and E_2° are given. The uncertainty of k_2 and k_4 is 5–10% and for k_{het} [eqn. (3)] ≈20%. The differences between the rate constants of the cleavage of the benzylic groups are not great; they go however in the expected direction. Compared with BTP^+, k_2 of both $ClBTP^+$ and $MOBTP^+$ are higher. This is in accordance with the general observation that both electron-donating and electron-withdrawing substituents stabilize aromatic radicals, which should

Table 1. Potentials (V vs. Ag/AgI in DMF–0.2 M $TBABF_4$) of the first and second reductions of some 1-substituted 2,4,6-triphenylpyridinium perchlorates, the rate of cleavage of the product from the first reduction (the radical) k_2, and of the product from the second reduction (the anion), k_4, together with the apparent heterogeneous rate constant for the second reduction. The reduction potential of 2,4,6-triphenylpyridine was −1.603 V vs. Ag/AgI.

R	k_2/s^{-1} (DPSC)	E_1°/V $PyR^+/PyR^\bullet$	E_2°/V $PyR^\bullet/PyR^-$	k_{het}/cm s^{-1} $PyR^\bullet/PyR^-$	k_2/s^{-1}	k_4/s^{-1}
Isopropyl	1±0.2	−0.43	−0.88	0.5	0.8	0.6
Benzyl	100±20	−0.42	−0.97	0.2	115	90
4-Methylbenzyl	100±20	−0.42	−0.98	0.15	110	50
4-Chlorobenzyl	250±30	−0.42	−0.93	0.1	275	70
4-Methoxybenzyl	160±30	−0.42	−0.98	0.1	145	140
Allyl	70±20	−0.42	−0.95	1	90	80
Phenyl	–	−0.48	−0.61	–	–	–
Methyl	–	−0.54	−0.98	–	–	–

make the radical a better leaving group. When comparing k_4, differences are found for which an explanation is not obvious; a chloro substituent usually helps to distribute the negative charge and thus stabilize the anion $ClBTP^-$ and making k_4 lower, as observed, but it also stabilizes the leaving group which should make the cleavage faster. The electron-donating methoxy group in $MOBTP^-$ has the opposite effect; the leaving group is destabilized, but the cleavage is faster. The differences are not large, but they seem to be larger than the uncertainty of the simulation of the experimental curves. The result is that the difference between k_2 and k_4 is greatest for $ClBTP^+$ and smallest for $MOBTP^+$ with BTP^+ being intermediate.

The unexpected finding that $k_2 > k_4$ might be understood if it is assumed that the phenyl groups in the 2 and 6 positions in the pyridinium compound and the radical are close to being perpendicular to the pyridine ring and thus not conjugated with the electron-accepting π-system; this could be caused by steric hindrance from the 1-substituent being in the plane of the pyridine ring. If the 1-substituent in the anion was out of this plane, due to the change in hybridization at the nitrogen atom, then the 2- and 6-phenyl groups could come into conjugation with the central π-system which might stabilize the negative charge of the anion by distributing it over a larger system. Such a change in conformation seems to be supported by the following two arguments.

The apparent heterogeneous rate constant, k_{het}, of the second reduction is smaller than those of the first and third reduction. A crude estimation of the Frumkin correction,[13,14] assuming no specific adsorption of the neutral radical, suggests that the standard heterogeneous rate constant is approximately five times greater than the apparent one. Even taking this correction into account k_{het} of the second reduction is smaller than those of the first and third reductions. This could be connected with a greater change in the conformation on going from the radical to the anion than on going from the pyridinium compound to the radical as suggested above.

According to calculations of the conformations of the radical $BTP^\bullet$ and the anion BTP^- using AM1 semiempirical MO calculations[15,16] the plane of the phenyl groups in the 2 and 6 positions of $BTP^\bullet$ are close to being perpendicular to the pyridine ring and the methylene group of the benzyl group close to being in the plane of the pyridine ring (Fig. 3). The figure has the pyridine ring in the centre, and the molecule is orientated so the C-2 (or C-6) phenyl group is seen as a plane; from the figure it is obvious that if the calculation gives a fair representation of the radical then there is no conjugation between the phenyl groups in the 2 and 6 positions and the pyridine ring. It is also seen, that the methylene group is only slightly out of the plane of the pyridine ring.

The dihydropyridine ring in BTP^- is close to being planar, but is not quite so; the carbon atoms 2, 3, 5 and 6 are in a plane which here will be referred to as the plane of the dihydropyridine ring (Fig. 4). The molecule is orientated in Fig. 4 so the plane of the dihydropyridine ring

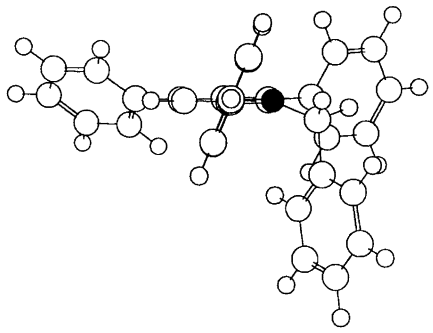


Fig. 3. Conformation of 1-benzyl-2,4,6-triphenylpyridine radical according to AM1 semiempirical MO calculations; the black atom is the nitrogen in the pyridine ring.

is perpendicular to the plane of the paper, again with the dihydropyridine ring in the centre. The figure shows that the planes of the phenyl groups in the 2, 4 and 6 positions are all slightly out of the plane of the dihydropyridine, but the angle between the planes is about the same as the angle between the phenyl groups in biphenyl and should not hinder a significant overlap of the π-electron systems. The methylene group is seen to be so much out of the central plane that it does not interfere significantly with the phenyl groups.

These calculations thus support the assumption that there is much less conjugation of the phenyl groups in the 2 and 6 positions with the central π-electron system in the radical than in the anion and that this is part of the explanation for the lower rate of cleavage of the anion compared with the radical; it also supports the hypothesis that the lower rate of heterogeneous electron transfer to the radical is connected with the relatively large change in conformation on going from the radical to the anion compared with the change in conformation on going from the pyridinium salt to the radical.

With regard to the *C*-alkylation of BTP^+ in the reaction with nitronate ions the aim of this investigation was not to elucidate the mechanism of the reaction; however, the results confirm the previous findings[6,7] that the reaction is not an outer-sphere electron transfer, and that

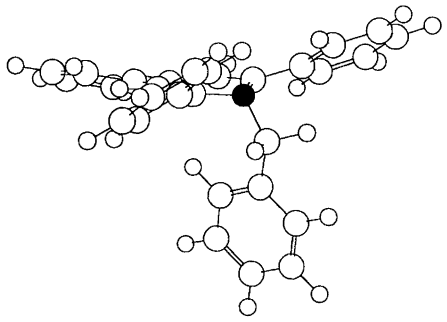


Fig. 4. Conformation of the anion of 1-benzyl-1,4-dihydro-2,4,6-triphenylpyridine according to AM1 semiempirical MO calculations; the black atom is the nitrogen atom in the pyridine ring.

C-alkylation of nitronate ions in a nucleophilic substitution is not necessarily an ET reaction. It might also be recalled that the addition of nitronate ion to activated olefins in the Michael reaction results in *C*-alkylation.

Experimental

Compounds. The 1-substituted 2,4,6-triphenylpyridinium salts were prepared by letting the required amine react with 2,4,6-triphenylpyrylium perchlorate following the procedure of Katritzky.[17]

Simulation program. ELEC is a general program for simulation of cyclic voltammetry.[18]

Reduction of 1-benzyl-2,4,6-triphenylpyridinium perchlorate. The reduction was performed in a conventional three-electrode H-cell also equipped with a glassy carbon rotating disc electrode (RDE); the cathode consisted of either a mercury pool or a platinum net. From the steady-state curve of the RDE the potential was set just after the first reduction wave (− 0.5 V vs. Ag/AgI). The reduction was stopped several times while a steady-state curve was obtained with the RDE ($v = 100$ mV s^{-1}). The height of the first wave decreased linearly with consumed coulombs according to a consumption of one electron per molecule. The ratio between the height of the first and second peak remained constant during the reduction, whereas the height of the third peak remained constant during the reduction, corresponding to the production of one molecule of TP for every molecule of substrate reduced. The solvent was either DMF or MeCN–0.2 M $TBABF_4$. When the reduction was finished, the solvent was diluted with an equal amount of water and, after cooling, extracted three times with diethyl ether. The collected ether fractions were washed three times with water. The yellow colour observed during the reaction was also seen in the ether extract, but after it had been dried over $MgSO_4$ for at least 4 h, the colour had almost disappeared. This suggests products of the type obtained in reaction (14); such compounds are known to be coloured and unstable. To ascertain that the colour did not originate from any amines derived from the DMF, we also performed reductions in MeCN, but in this solvent the observed colour was even more intense. A comparison of the product distributions, as analysed by GC and GC–MS, for reductions performed in the two solvents revealed no differences, which supports the theory that the colour is due to the presence of small amounts of unstable species. The main products were 2,4,6-triphenylpyridine in nearly quantitative yield and bibenzyl in varying yield; toluene was not found by GC, but it is difficult to exclude the possibility that some toluene was lost during the electrolysis or work-up; on GC–MS two peaks with an m/z value corresponding to benzylated bibenzyls were detected in low yield. No products were found by GC or GC–MS which could account for the somewhat low material balance of the benzyl part of the cleavage.

In order to ascertain that no benzylmercury compounds were formed, we also used a platinum net as the cathode. This had no effect on the product distribution. An initial addition of TP had no effect on the amount of bibenzyl observed. Initial addition of bibenzyl resulted in only a small increase in the amount of benzylated bibenzyl.

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